# **ORGANOMETALLICS**

# Ethylene Reactions of a $[ReH(\eta^2-BH_4)(NO)(PPh_3)_2]$ Complex: Reductive Elimination of Ethane and Oxidative Coupling to Butadiene

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**Supporting Information** 

**ABSTRACT:** The borohydride complex  $[\text{Re}^{+I}H(\eta^2-\text{BH}_4)(\text{NO})-(\text{PPh}_3)_2]$  (**1ph**) reacts with ethylene to yield  $[\text{Re}^{+I}\text{H}_2(\eta^2-C_2\text{H}_4)(\text{NO})(\text{PPh}_3)_2]$  (**2ph**) and triethylborane formed by ethylene hydroboration. Subsequent ethylene insertion into the Re–H bond of **2ph** and uptake of another 1 equiv of ethylene led to the kinetically stable *cis*-hydrido–ethyl complex  $[\text{Re}^{+I}\text{H}(\text{Et})-(\eta^2-C_2\text{H}_4)(\text{NO})(\text{PPh}_3)_2]$  (**3ph**). **3ph** was found to slowly reductively eliminate ethane. The rate of this process was



determined by quantitative NMR spectroscopy in the temperature range from 293 to 338 K, enabling calculation of the activation parameters ( $\Delta H^{\ddagger} = 68.7 \text{ kJ mol}^{-1}, \Delta S^{\ddagger} = -94 \text{ J mol}^{-1} \text{ K}^{-1}$ ; half-life time 1.8 h at 303 K). The reaction was found to follow first-order kinetics in  $c(3\mathbf{ph})$  and is zeroth order in  $c(C_2H_4)$  and  $c(PPh_3)$ , ruling out preceding ligand dissociation. The presumptive intermediate  $[\text{Re}^{-1}(\eta^2-C_2H_4)(\text{NO})(\text{PPh}_3)_2]$  could not be traced, since it rapidly reacted further with ethylene, furnishing the stable butadiene complex  $[\text{Re}^{-1}(\eta^2-C_2H_4)(\eta^4-C_4H_6)(\text{NO})(\text{PPh}_3)]$  (**4ph**) in 88% yield. This transformation of dehydrogenative ethylene coupling is suggested to involve the elementary steps of rhenacyclopentane formation from two coordinated ethylene ligands and then double C–H activation via  $\beta$ -hydride shifts to generate the butadiene unit and formal H<sub>2</sub> elimination from the rhenium dihydride with concomitant triphenylphosphine elimination. An X-ray crystallographic study confirmed the spectroscopically derived pentacoordinate structure of **4ph**.

# 1. INTRODUCTION

Our efforts to develop rhenium nitrosyl based hydrogenation catalysts culminated in recent reports on highly efficient olefin hydrogenation catalyzes with  $[ReHX(L)(NO)(PR_3)_2]$  (X = F, Cl, Br, I; R = cy, *i*Pr) and [ReHBr(L)(NO)(P $\cap$ P)] (P $\cap$ P = dpephos, homoxantphos, Sixantphos, dppfc, diprpfc) catalysts.<sup>1</sup> In both cases of catalyses the reaction courses were found to proceed along Osborn type cycles<sup>2</sup> involving Re(+I)/Re(+III)redox changes. The alkane release steps of these catalyses were indeed reductive eliminations from a Re<sup>+III</sup>(H)(alkyl) species. In contrast, the previously reported [ReH<sub>2</sub>(olefin)(NO)- $(PR_3)_2$  (R = cy, *iPr*) systems<sup>3</sup> were suggested to follow catalytic routes involving either Re(+I)/Re(+III) or Re(+I)/ Re(-I) redox changes (Scheme 1). This capability to generate redox couples at different oxidation state levels makes rhenium very prone to hydrogenations with significantly differing coordination spheres. This gave us the notion to study the reactions of  $[\text{ReH}(\eta^2\text{-BH}_4)(\text{NO})(\text{PPh}_3)_2]$  (1ph) with ethylene in greater detail in order to explore its potential further to establish high- or low-oxidation-state routes. The propensity of rhenium centers to adopt various oxidation states in hydrogen and olefin chemistry is, for instance, also reflected in a  $[\operatorname{ReH}_{7-n}L_{n/2}(L')_2]$  series<sup>4</sup> with one to seven hydrides. Such hydride species are often subject to catalytically relevant  $\operatorname{Re}^{n}(\operatorname{H})_{2} \leftrightarrows \operatorname{Re}^{n-2}(\eta^{2}-\operatorname{H}_{2})$  redox equilibria<sup>5,4a</sup> and are additionally known for their high olefin affinity.<sup>6</sup> In view of the ligand tuning we anticipated that the redox properties of catalytic rhenium centers prone to hydrogen and olefin chemistry could

Scheme 1. Generalized Re(+I)/Re(-I) and Re(+I)/Re(+III)Hydrogenation Schemes for  $\text{ReH}_2(\text{olefin})$  Complexes<sup>*a*</sup>



 $a \square$  = vacant coordination site or labile ligand.

be additionally fine-tuned by the type of phosphine substitution pattern, as for example in the case of the  $[{\rm ReH_7}({\rm PR_3})_2]$  system, which is known to respond to subtle changes in the phosphine stereoelectronic properties.<sup>4,5a</sup> Moreover, we expected that on the basis of the donicities and steric demand of the phosphine ligands, they should show also different catalytically relevant dissociation behavior. Variations in the phosphine coordination sphere could therefore open up additional catalytic reaction channels, such as dehydrogenation,<sup>7</sup> C–H activation,<sup>8,4b</sup> and C–C bond formation<sup>9</sup> pathways. To illustrate this important

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Figure 1. <sup>1</sup>H NMR spectrum of a mixture of 2ph and 3ph (THF- $d_8$ , 500 MHz, 300 K). The ethylene ligands are fixed in an "upright" conformation aligned with the P–Re–P axis.

point of "catalytic" rhenium, the anticipated two routes of olefin hydrogenations with Re(-I/+I) or Re(+I/+III) centers are sketched in Scheme 1 in generalized form for a  $\text{Re}(H)_2(\text{olefin})$  moiety.

The reactions of the tricyclohexylphosphine and triisopropylphosphine derivatives  $[\text{ReH}(\eta^2\text{-BH}_4)(\text{NO})(\text{PR}_3)_2]$  (R = cy (**1cy**), R = *i*Pr (**1***i***Pr**)) with ethylene were studied earlier and furnished access to the stable dihydride olefin complexes  $[\text{ReH}_2(\eta^2\text{-}\text{C}_2\text{H}_4)(\text{NO})(\text{PR}_3)_2]$  (R = cy (**2cy**), *i*Pr (**2***i***Pr**)),<sup>3</sup> which corresponded to a substitution process replacing the BH<sub>3</sub> unit as BH<sub>3</sub>·THF and a slightly modified pathway along the Re(+I)/Re(+III) cycle of Scheme 1 and according to Scheme 2.

The reaction apparently stopped at the olefin dihydride level, which we attributed to the strongly donating property of the phosphine ligands. The rhenium centers were thought to be too electron rich, preventing the  $\beta$ -hydride shift to form an ethyl group and subsequent reaction steps from this point. We therefore anticipated that the less donating triphenylphosphine substituent would be more supportive for a subsequent reaction chemistry, eventually turning with less electron rich centers into a Re(-I/+I) chemistry and in addition potentially permitting also dissociation of a less strongly bound triphenylphosphine.

# 2. RESULTS

The reaction of **1ph** with ethylene was found to proceed in THF at 23 °C via the unstable intermediates  $[\text{Re}^{+1}\text{H}_2(\eta^2-C_2\text{H}_4)(\text{NO})(\text{PPh}_3)_2]$  (**2ph**) and  $[\text{Re}^{+1}\text{H}(\text{Et})(\eta^2-C_2\text{H}_4)(\text{NO})-(\text{PPh}_3)_2]$  (**3ph**) to eventually generate the stable dehydrogenative ethylene coupling product  $[\text{Re}(\eta^2-C_2\text{H}_4)(\eta^4-C_4\text{H}_6)(\text{NO})-(\text{PPh}_3)]$  (**4ph**) (Scheme 4). **2ph** and **3ph** were characterized in situ by <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR and IR spectroscopy in solution.

2.1. Reaction of 1ph with Ethylene Forming 2ph and 3ph. The less donating PPh<sub>3</sub> of the 1ph derivative was seen to reveal initially a reactivity similar to that of the 1cy and 1*i*Pr derivatives but then showed follow-up chemistry. The reaction of 1ph with ethylene dissolved in deuterated benzene or THF was initially studied by in situ NMR spectroscopy. In the  ${}^{31}P{}^{1}H{}$  NMR spectrum the signal of the starting material at 33 ppm disappeared and new signals emerged first at 28 ppm

(2ph) and subsequently at 22 ppm (3ph). The rates of the interconversions of 1ph into 2ph and then into 3ph were found to be strongly dependent on the ethylene concentration and the solvent. The ethylene concentration could not reproducibly be controlled in the NMR tube, which prevented quantitative investigations. However, the conversion of 1ph to 2ph was found to be much faster in THF than in benzene, and therefore it seemed reasonable to assume that THF facilitates BH<sub>3</sub> dissociation from 1ph, generating an unsaturated or THFstabilized rhenium intermediate, both of which could not be traced spectroscopically (Scheme 4). This also suggested that in the formation of 2ph BH<sub>3</sub> dissociation was rate limiting. Subsequently **2ph** transformed into **3ph** by a  $\beta$ -hydrogen shift step followed by the coordination of another 1 equiv of ethylene. The rate of this transformation is comparable to the rate of 2ph formation. Thus, after exposure of 1ph to ethylene at ambient temperature both species 2ph and 3ph were present in the reaction mixture for a short period of time within about 3-10 min. **3ph** becomes the sole product, depending strongly on the C<sub>2</sub>H<sub>4</sub> pressure and the mixing process. Quick removal of the ethylene atmosphere and of BH<sub>3</sub>/BEt<sub>3</sub> in vacuo after completion of the transformation of 1ph into 2ph stopped the conversion of 2ph into 3ph and allowed <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR and IR spectroscopic characterization of **2ph** in the 2ph/3ph mixture. From this observation we concluded that the driving force for the  $2ph \rightarrow 3ph$  conversion is the trapping of the unsaturated  $[ReH(Et)(NO)(PPh_3)_2]$  intermediate by ethylene coordination, since otherwise this intermediate would be expected to exist even in the absence of ethylene. Thus, we can state that the 16e complex  $[ReH(Et)(NO)(PPh_3)_2]$  is thermodynamically less favored than the 18e complexes 2ph and 3ph. 2ph and 3ph possess distinct <sup>31</sup>P{<sup>1</sup>H} NMR spectra, and their  ${}^{1}H$  and  ${}^{13}C{}^{1}H$  spectra differ in the Re–H, Re–Et, and Re– $(\eta^2$ -C<sub>2</sub>H<sub>4</sub>) chemical shift regions, whereas the <sup>1</sup>H and  ${}^{13}C{}^{1}H{}$  signals of the PPh<sub>3</sub> ligands were seen to coincide. In the <sup>1</sup>H NMR spectrum of 2ph in THF of Figure 1 the chemically different rhenium hydrides gave rise to a set of signals at 1.51 (td,  ${}^{2}J_{PH} = 36.5$  Hz,  ${}^{2}J_{HH} = 7.4$  Hz) and -3.29 ppm (td,  ${}^{2}J_{PH} = 27.6$  Hz,  ${}^{2}J_{HH} = 7.4$  Hz). The protons of the ethylene ligand were found to be also chemically different and

therefore gave rise to two multiplets at 2.84 ppm (2H) and at 2.76 ppm (2H). These multiplets were broadened at room temperature (300 K, 500 MHz). Increasing the temperature of the sample to 320 K led to coalescence, which would be consistent with a low barrier for ethylene rotation around the Re– $(\eta^2$ -C<sub>2</sub>H<sub>4</sub>) axis. In the <sup>31</sup>P NMR spectrum a broad virtual triplet at 28.5 ppm originating from similar couplings to both the Re–H moieties is observed, which suggests a symmetrical trans phosphine arrangement, in agreement with its structure sketched in Scheme 4. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum the <sup>13</sup>C<sub>ethylene</sub> nuclei cause one signal at 35.8 ppm. The assignment of this carbon signal to the ethylene ligand was confirmed by a HSQC experiment.

The <sup>1</sup>H NMR spectrum of **3ph** also displayed in Figure 1 consists of two isolated spin systems attributed to the ethylene and the ethyl ligands and a H<sub>Re</sub> signal. This latter signal at 2.91 ppm (t,  ${}^{2}J_{PH}$  = 31.8 Hz, 1 H) shows the typical coupling pattern originating from the coupling with two chemically equivalent phosphorus nuclei. The methylene protons of the Re-Et unit entailed a broadened resonance at -1.17 ppm (q,  ${}^{3}J_{HH} = 7.3$ Hz, 2 H). Phosphorus decoupling furnished a sharp quartet. The adjacent Me group was found to cause a well-defined signal at 0.68 ppm (t,  ${}^{3}J_{HH} = 7.3$  Hz, 3 H). The four protons of the ethylene ligand were observed as two broad resonances, which resolve in the  ${}^{1}H{}^{31}P$  NMR spectrum into a set of two sharp resonances at 2.94 ppm (d,  $J_{\rm HH}$  = 10.2 Hz, 2 H) and at 2.12 ppm (d,  $J_{HH}$  = 10.2 Hz, 2 H). These ethylene signals are not affected by dynamic exchange processes, indicating hindered rotation of the ethylene ligand in a presumably preferred "upright" conformation aligned with the P-Re-P axis as the preferred rotameric conformation. This could be confirmed applying a HSQC experiment, where both signals were assigned to one <sup>13</sup>C resonance at 42.9 ppm. In this experiment the methylene and the methyl protons of the Et group expectedly showed correlation with two <sup>13</sup>C resonances at 19.0 and 20.0 ppm. In the <sup>31</sup>P NMR spectrum of **3ph** a broad signal was observed at 20.4 ppm (d,  ${}^{2}J_{PH} = 31.8$  Hz). From these data, it was also concluded that the phosphines are bound in chemically equivalent trans positions. However, the relative arrangement of the ethylene, the ethyl, and the hydride ligands within the pseudo-octahedral environment could not be fully elucidated. Therefore more detailed NMR experiments were carried out assuming the three constitutional isomers A, B, and C (Scheme 3) as a basis for the interpretation of a NOESY spectrum of 3ph.

Scheme 3. The Three Possible Trans Phosphine Isomers of 3ph



For the "equatorial" ligands the trans influence<sup>10</sup> decreases in the order NO >  $C_2H_4$  > H > Et, from which we could predict that **A** is more likely than **B** and **C**, since only in isomer **A** is the strongest trans ligand (NO) trans to the weakest trans ligand (Et). The presence of cross-peaks in the NOESY spectrum showed correlation of the Me protons of the ethyl ligand and the hydride ligand and cross-peaks between the methylene protons of the ethyl ligand showed correlation with those of the ethylene ligand, which undoubtedly supports that isomer **A** is the structure of **3ph**. On actual reaction of **2ph** with ethylene via a  $\beta$ -hydride shift and ethylene addition to the vacant site, the stereochemistry of this process would be expected such that the isomer **C** is created. Therefore, we have to assume an intermittent Et group rearrangement changing sides and final ethylene addition to form isomer **A** of **3ph** (Scheme 4).

2.2. Reductive Elimination of Ethane from 3ph and Dehydrogenative Ethylene Coupling To Form 4ph. Unlike 2ph, 3ph was found to be remarkably stable in solution at room temperature. 3ph seemed to decompose by initial ethane reductive elimination, which however occurred only very slowly (half-life time 1.8 h at 303 K). This encouraged us to investigate the kinetics of of this process in the presence of ethylene in greater detail. Expectedly, the reductive elimination rate was found to depend first order on c(3ph) but was independent of  $c(C_2H_4)$  and the type of solvent (benzene or THF). Also, no influence of  $c(PPh_3)$  could be determined, which changes during the reaction course due to PPh<sub>3</sub> release concomitant with the formation of 4ph. Thus, the reductive elimination is not induced by preceding ethylene or phosphine ligand dissociation. We decided to determine the rates of the reductive elimination at temperatures ranging from 293 to 338 K via <sup>1</sup>H NMR spectroscopy and integration of the 3ph methylene protons with the PPh<sub>3</sub> signals as internal standard. This also allowed determination of the activation parameters of this process ( $\Delta H^{\ddagger} = 68.7 \text{ kJ mol}^{-1} \Delta S^{\ddagger} = -94 \text{ J mol}^{-1} \text{ K}^{-1}$ ) via an Eyring plot (Figure 2).<sup>11</sup> The fact that reductive elimination occurs further supports the earlier proposed structure of 3ph featuring a cis-hydrido-alkyl arrangement, since trans positions of the eliminating moieties would not permit reductive eliminations.12

Alongside with the reductive elimination of ethane, the formation of the butadiene ligand in 4ph was observed. For this transformation we propose a mechanism as depicted in Scheme 4 proceeding via the formation of the bis(ethylene) complex  $[\text{Re}^{-I}(\eta^2-C_2H_4)_2(\text{NO})(\text{PPh}_3)_2]$  followed by coupling of the ethylene ligands to form a redox-driven [Re<sup>+1</sup>( $\eta^2$ -C<sub>4</sub>H<sub>8</sub>)(NO)- $(PPh_3)_2$  molecule with a metallacyclopentane unit and concomitant oxidation to a 16e rhenium center. From this Re(+I) species facile double  $\beta$ -hydride shifts are expected to occur, along with H<sub>2</sub> loss or perhaps hydrogenation of an ethylene ligand with subsequent uptake of C<sub>2</sub>H<sub>4</sub> to produce 4ph. None of these intermediates could be traced in the NMR spectra of the reaction mixture, which points to their high reactivity. Analytically pure samples of 4ph were obtained via the reaction of **1ph** in THF in the presence of  $C_2H_4$ . Isolation was accomplished via filtration of the reaction solution and evaporation of the volatiles, followed by extraction of the oily residue with hexane in 88% yield. 4ph was characterized by elemental analysis, IR and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The <sup>1</sup>H NMR spectrum of **4ph** consisted of PPh<sub>3</sub> signals in the aromatic region and of two spin systems, which could be assigned by means of COSY, HSQC, and HMBC spectra to the butadiene and the ethylene ligands (Scheme 5). In the  ${}^{13}C{}^{1}H$  NMR spectrum of **4ph**, the PPh<sub>3</sub> ligand gave rise to the expected aromatic carbon signals in the region of 125-140 ppm. The four chemically different C<sub>butadiene</sub> nuclei and the two chemically different C<sub>ethylene</sub> nuclei were assigned by aid of HSQC and HMBC experiments as well, as depicted in Scheme 5. The signals of the terminal butadiene carbon nuclei and of the ethylene carbon atoms showed coupling with the Scheme 4. Reaction of 1ph with C<sub>2</sub>H<sub>4</sub>





**Figure 2.** Eyring plot of the reductive elimination of ethane from 3f in benzene- $d_{6}$ .

Scheme 5. Assignment Scheme of the <sup>1</sup>H and <sup>13</sup>C Signals of 4ph (C<sub>6</sub>D<sub>6</sub>, 500 MHz, 300 K)



phosphorus nucleus (3–7 Hz), whereas for the internal carbon atoms this coupling was absent. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum **4ph** gave rise to a single resonance at 22.4 ppm and the IR spectrum an intense and sharp  $\nu$ (NO) band was observed at 1641 cm<sup>-1</sup>.

The butadiene or the ethylene ligands of the pentacoordinate  $d^8$  system did not show NMR dynamics at room temperature as is known for other butadiene complexes.<sup>13</sup> Therefore, these ligands were assumed to be strongly bound in a unique, highly asymmetric conformer, which is stable at room temperature. Three different s-cis butadiene rotamers of **4ph** are principally conceivable as structural isomers (Scheme 6). In addition, metallacyclopentene structures and an *s-trans-* $\eta^4$ -butadiene complex could be envisaged as well (Scheme 6).

The formation of an s-trans butadiene complex could be ruled out by a NOESY experiment, which confirmed the spacial proximity of the  $H_{syn1}$  and  $H_{syn2}$  protons. Furthermore, the geminal coupling between the syn and the anti protons is only 3 Hz, suggesting sp<sup>2</sup> rather than sp<sup>3</sup> carbon atoms,<sup>14</sup> which

Scheme 6. "Top View" of the Three Conformers of 4ph



made the metallacyclopentene structure seem unlikely. In accordance with this, all vicinal coupling constants are approximately 7 Hz, which indicates that the butadiene ligand is  $\eta^4$  rather than  $\eta^2$  bound, as otherwise the coupling pattern in a metallacyclopentene envelope structure would lead to different coupling constants<sup>15</sup> for the internal and the two types of terminal protons. In accord with that, we propose a s*cis*- $\eta^4$ -butadiene structure for **4ph**. In addition, we could also rule out rotamer F, as in the NOESY experiment cross-peaks between the ethylene multiplet at 1.66 ppm and the H(int1)/H(anti1) atoms are visible. This indicated that 4ph possesses either the structure of rotamer D or rotamer E. DFT calculations on the PMe<sub>3</sub> model rotamers of  $[\text{Re}(\eta^2 C_2H_4)(\eta^4$ -butadiene)(NO)(PMe\_3)]  $D_{Me}-F_{Me}$  in ref 16 revealed that the  $E_{Me}\xspace$  rotamer is expected to be thermodynamically 16.3 kJ mol<sup>-1</sup> more favorable than the  $F_{Me}$  rotamer and 36.0 kJ mol<sup>-1</sup> more favorable than the  $D_{Me}$  rotamer. To gain further insight into the structure of 4ph, an X-ray diffraction study was carried out. The ORTEP diagram in Figure 3 indeed showed that (a) the butadiene ligand possesses an s-cis conformation, which could be derived from the <sup>1</sup>H NMR NOESY spectrum and the <sup>1</sup>H NMR coupling patterns, and (b) the ethylene and the butadiene ligands are arranged as was proposed from the NOESY spectrum. Additionally the structure of 4ph possesses conformation E (Scheme 6) with the PPh<sub>3</sub> ligand in the "leg in the hole" position of the butadiene ligand.15



Figure 3. ORTEP diagram of 4ph drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å): C1-C2 = 1.433(5), C3-C4 = 1.428(5), C4-C5 = 1.404(6), C5-C6 = 1.444(6), C1-Re1 = 2.210(3), C2-Re1 = 2.214(3), C3-Re1 = 2.229(3), C4-Re1 = 2.233(3), C5-Re1 = 2.263(4), C6-Re1 = 2.260(3), N1-O1 = 1.200(3), N1-Re1 = 1.773(2), P1-Re1 = 2.4025(7). Selected bond angles (deg): C3-C4-C5 = 116.1(3), C4-C5-C6 = 118.2(3), C1-Re1-C3 = 145.86(13), C1-Re1-C6 = 85.48, C3-Re1-N1 = 101.90(13), C6-Re1-N1 = 167.33(12), C2-Re1-P1 = 86.42(9), C3-Re1-P1 = 85.26(9), C6-Re1-P1 = 94.40(9), O1-N1-Re1 = 177.0(2).

A closer look into the structure of **4ph** revealed that all Re– C bonds are in the range of 2.210–2.263 Å, which is typical for Re–C single bonds. The C–C bond lengths (1.404-1.444 Å)are between single (1.53 Å) and double bonds  $(1.34 \text{ Å})^{17}$  and thus indicate strong (back) bonding<sup>18</sup> in this Re(–I) system. Furthermore, the very uniform C–C bond lengths in the butadiene ligand speak for strong electron delocalization. The NO ligand is almost linearly bound ( $\angle O1-N1-Re1 =$  $177.0(2)^{\circ}$ ) and thus acts as a 3e ligand with typically short Re–NO (1.773(2) Å) and elongated N–O (1.200(3) Å) bonds, also indicating strong back-donation from the electron rich Re(–I) center. Overall the structure can be described as a trigonal pyramid with the NO, ethylene, and butadiene ligands in the basal plane and the phosphine ligand in an apical position.

**2.3. Attempts To Catalyze Dehydrogenative Ethylene Coupling Forming Butadiene.** We also probed the capability of **4ph** to catalyze dehydrogenative ethylene coupling along eq 1 as occurs stoichiometrically in the formation of **4ph**. The ethylene side of eq 1 is thermodynamically favored by  $\Delta H = -5.2$  kJ mol<sup>-1.17</sup> The entropy  $\Delta S$  for eq 1 should be close to 0. Therefore, coupling of this reaction with hydrogenation of either ethylene ( $\Delta H = -136.3$  kJ mol<sup>-1</sup>) or butadiene ( $\Delta H = -108.4$  kJ mol<sup>-1</sup>) would generate a more negative free enthalpy driving force, sufficiently high for exergonic dehydrogenative ethylene coupling.<sup>17</sup>

$$2C_2H_4 \rightleftharpoons H_2 + C_4H_6 \tag{1}$$

Pursued by NMR, the reaction of **4ph** in THF solutions with ethylene (2 bar) did not show free butadiene<sup>19</sup> even after 1 week of exposure at 60 °C. Employing even harsher conditions, charging with 60 bar of ethylene for 24 h at 100 °C (pressure rises to 100 bar), also did not result in  $C_4H_6$  release. While **4ph** was found to be stable at 60 °C under 2 bar of ethylene for 1 week, it decomposed under the more harsh conditions given, resulting in various unidentified decomposition products. The butadiene ligand in **4ph** is apparently quite strongly bound to the rhenium center, and its strong binding is presumably part of the thermodynamic driving force for the facile conversion to **4ph**. This stability, however, is thought to prevent the closing up of the catalytic cycle for dehydrogenative ethylene coupling (Scheme 4).

# 3. DISCUSSION

This study revealed major differences in reactivity between the phenyl derivative 1ph and the previously reported isopropyl/ cyclohexyl derivatives 1iPr/1cy of a  $[ReH(\eta^2-BH_4)(NO) (PR_2)_2$  complex series which are caused mainly by differences in the donor strengths of these ligands,<sup>20</sup> which to a certain extent also correlates with their binding strengths to the rhenium center. In the case of the reactions of the liPr/lcy complexes only exchange of the BH<sub>3</sub> moiety with ethylene could be initiated.<sup>3</sup> This stands in contrast to the reaction of 1ph bearing less donating triphenylphosphine ligands with ethylene, where the formation of 2ph is the starting point of a cascade of consecutive steps leading finally to oxidative ethylene coupling forming a butadiene ligand in 4ph. A decreased electron density in 1ph is illustrated by a  $\nu(NO)$ band at 1666  $cm^{-1}$  in comparison with the bands of liPr/lcyat 1660 cm<sup>-1</sup>, which indicated the right trend in electron richness of the rhenium centers, but the values are apparently an overlay of counteracting electronic effects and are in sum therefore too small to explain the differences in the observed reactivities. However, it is indeed expected that the direct influence of the different electron donicities of the phosphorus ligands and the accompanying electron densities at the rhenium centers trigger formation of the kinetically stable cis-hydridoalkyl complex 3ph in the reaction of 2ph with ethylene. Moreover, such cis-hydrido-alkyl species which are formed from a metal dihydride complex via migratory insertion of an olefin into a M-H bond are to our knowledge usually shortlived intermediates and are hardly traceable<sup>21</sup> because of the spontaneously occurring elimination of alkane. In contrast to this, numerous cis-hydrido-alkyl complexes of varying stabilities are known, which were formed by other reactions such as alkylation with, for example, Grignard compounds<sup>22</sup> or by protonation of alkyl complexes  $2^{3}$  or by the oxidative addition of a C-H bond to an unsaturated electron-rich metal as is known e.g. for numerous Ru, Rh, Pd, Os, Ir, and Pt complexes.<sup>24</sup> In the given case of triphenylphosphinesubstituted complexes the extraordinary stability of these species was attributed to a reduced tendency for reductive elimination of ethane, since an electron-rich Re(-I) state would be reached, for which any donor phosphine-even the comparably moderate donor strength of PPh3-substitution pattern would be counteracting. This is well reflected in the relatively high activation barrier for this process (e.g.,  $\Delta G^{\ddagger}$  = 96.7 kJ mol<sup>-1</sup> at 298 K), which is not rare for such processes.<sup>25</sup> These findings and earlier results<sup>1a,b</sup> support the idea that in the case of alternative reaction pathways Re(+III)/Re(+I) reductive eliminations are preferred over related Re(+I)/Re(-I)processes. However, another factor could influence this process as well: often reductive eliminations are initiated and accelerated by initial phosphine dissociation. It is a general experience in the realm of homogeneous catalysis that lower coordination numbers accelerate reductive eliminations and therefore the weaker the binding strength of a phosphine, the lower the minimal coordination number could be and the lower the activation barrier would be. The reduced electron donation of the triphenylphosphine ligand in 3ph might permit its dissociation and subsequently enhance reductive elimination in comparison with triisopropyl- or tricyclophexylphosphine.

However, the transformation of **3ph** to **4ph** has been found to be independent of  $c(PPh_3)$ , which indeed rules out this possibility.

The structure of the olefin/alkyl complex **3ph** can also be compared with those of low valent Ni-based olefin oligomerization/isomerization catalysts, for which *cis*-alkyl–ethylene complexes were proposed to be important intermediates.<sup>26</sup> However, olefin oligomerization was not observed during the NMR experiments in solutions of **3ph**, which we interpret in terms of a hindered alkyl migration onto bound ethylene. For this process the ethylene ligand of **3ph** had to be aligned with the NO, Et, H plane so that the relatively high barrier for the ethylene ligand rotation in **3ph** would add to the overall barrier of alky migration. Basically it is again an overly high electron density on the metal center which contributes in various ways to hindrance of repetitive olefin insertions in the chain propagation process of olefin polymerizations.<sup>26b,c</sup>

Nevertheless, the unsaturated intermediate  $[\text{Re}(\eta^2-\text{C}_2\text{H}_4) (NO)(PPh_3)_2$  complex resulting from ethane elimination of 3ph proved to be capable of an alternative reaction path. First, another ethylene adds to the rhenium center and in the dehydrogenative coupling of ethylene to butadiene a rhenacyclopentane is then formed, with release of H<sub>2</sub> and PPh<sub>3</sub> to eventually form 4ph after  $C_2H_4$  addition (Scheme 4). The oxidative coupling of ethane furnishing butadiene complexes is rather uncommon,<sup>27</sup> whereas reductive elimination of ethenyl moieties furnishing butadiene complexes or the synthesis of butadiene complexes by the reduction of a precursor complex in the presence of butadiene are wellknown.<sup>28</sup> In this reaction course hydride olefin intermediates are likely to be generated. It should be mentioned that this occurs somewhat analogously to catalytic cycles of Ni-based olefin oligomerizations,<sup>26</sup> where  $\beta$ -hydride shifts were seen to participate in the processes, as well. At the intermittent stage of the second  $\beta$ -hydride shift from the rhenacyclopentane, PPh<sub>3</sub> dissociation is required, another condition which makes it necessary to have a labile phosphine within the coordination sphere. It is also noteworthy that olefin oligomerization pathways via the metallacycloalkene route were postulated for Cr-based catalysts.<sup>29</sup> However, in the NMR pursuits to generate 4ph, neither a rhenacyclopentane species and elimination of butenes nor the formation of higher olefins could be observed. The thermodynamic driving force for the formation of 4ph is the strong butadiene binding to the rhenium center; for that reason the rhenium-based catalysis of dehydrogenative ethylene coupling apparently could not be achieved.

# 4. CONCLUSIONS

This study on the hydrogen–ethylene chemistry of triphenylphosphine nitrosyl rhenium complexes demonstrated that the complex  $[\text{Re}(\text{H})_2(\eta^2-\text{C}_2\text{H}_4)(\text{NO})(\text{PPh}_3)_2]$  (**2ph**) induces ethylene hydrogenation and was seen to yield ethane. This transformation follows the mechanistic lines of an Osborn type<sup>30</sup> olefin hydrogenation catalysis but was stoichiometric and much slower in the olefin insertion step to yield eventually the *cis*-hydrido–ethyl rhenium(+I) species **3ph**.<sup>1</sup> The relaxed positions of the trans-disposed monophosphines is thought to significantly contribute to the stabilization of **3ph**, but the retardation of this process is anticipated to be due to the destabilization of the final low oxidation state of the  $[\text{Re}^{-I}(\eta^2-C_2\text{H}_4)(\text{NO})(\text{PPh}_3)_2]$  species appearing after the rate-limiting reductive elimination of ethane. The subsequent diethylene  $[\text{Re}^{-I}(\eta^2-C_2\text{H}_4)_2(\text{NO})(\text{PPh}_3)_2]$  intermediate reacted instantaneously with further ethylene uptake to the ethylene butadiene Re(-I) complex **4ph**. This revealed an unexpected facet of Re(-I/+I)NO chemistry, demonstrating reactivity closely related to those of chromium-based olefin oligomerization catalysts<sup>29</sup> encompassing oxidative coupling of ethylene by metallacyclization, double  $\beta$ -hydride elimination steps, and reductive elimination of an H<sub>2</sub> equivalent. The availability of the given redox-driven steps was attributed to the medium strength in donicity of PPh<sub>3</sub> still permitting access to highly reduced Re(+I) species and providing a labile phosphine for vacant sites required at some stages of the transformations. The application of the PPh<sub>3</sub> ligand can thus be viewed as part of a rhenium-based tuning effort, which specifically opened up the quite unusual reaction channel of dehydrogenative ethylene coupling.

### 5. EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out under an atmosphere of dry nitrogen using either standard Schlenk techniques or an MBraun glovebox. All solvents were dried, distilled, and degassed according to standard laboratory procedures. [ReH( $\eta^2$ -BH<sub>4</sub>)(NO)(PPh<sub>3</sub>)<sub>2</sub>] was prepared according to published methods<sup>31</sup> and stored at -30 °C. NMR spectra were recorded on a Bruker AV-2 500 spectrometer. Chemical shifts are expressed in parts per million (ppm) and referenced to the solvent's residual signals<sup>32</sup> or in the case of <sup>31</sup>P{<sup>1</sup>H} NMR spectra to an external standard (85% H<sub>3</sub>PO<sub>4</sub> at  $\delta$  0.0 ppm). IR spectra were recorded on a BioRad Excalibur spectrometer. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zürich.

[ReH<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(NO)(PPh<sub>3</sub>)<sub>2</sub>] (2ph) and [ReH(Et)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(NO)-(PPh<sub>3</sub>)<sub>2</sub>] (3ph). In an NMR tube with a Young Teflon cap a suspension of [ReH( $\eta^2$ -BH<sub>4</sub>)(NO)(PPh<sub>3</sub>)<sub>2</sub>] (0.010 g, 0.0013 mmol) in C<sub>6</sub>D<sub>6</sub> (0.6 mL) or alternatively THF (0.6 mL) was degassed using three freeze-pump-thaw cycles before the tube was charged with ethylene (1–2 bar). The NMR tube was shaken vigorously. The sample so prepared was used for NMR spectroscopic characterization of 2ph and 3ph. For IR spectroscopy the volatiles were quickly removed in vacuo and the oily residue was used directly for the preparation of a KBr pellet.

NMR Spectroscopic Data of [ReH<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(NO)(PPh<sub>3</sub>)<sub>2</sub>] (**2ph**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, 500 MHz): δ 7.86 (m, 12 H, PPh<sub>3</sub>), 7.25–6.90 (m, 18 H, PPh<sub>3</sub>), 2.84 (m, 2 H, C<sub>2</sub>H<sub>4</sub>), 2.76 (m, 2 H, C<sub>2</sub>H<sub>4</sub>), 1.51 (td, J<sub>PH</sub> = 36.5 Hz, J<sub>HH</sub> = 7.4 Hz, 1 H, ReH), -3.29 (td, J<sub>PH</sub> = 27.6 Hz, J<sub>HH</sub> = 7.4 Hz, 1 H, ReH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K, 125 MHz): δ = 136.9 (t, J<sub>PC</sub> = 25.0 Hz, PPh<sub>3</sub>), 134.6 (t, J<sub>PC</sub> = 5.0 Hz, PPh<sub>3</sub>), 130.0, 128.2–127.5 (m, PPh<sub>3</sub> and C<sub>6</sub>D<sub>6</sub>), 35.8 (s, C<sub>2</sub>H<sub>4</sub>) ppm. <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, 200 MHz): δ 28.5 (dd, J<sub>HP</sub> = 36.5 Hz, J<sub>HP</sub> = 27.6 Hz, PPh<sub>3</sub>) ppm.

NMR Spectroscopic Data of [ReH(Et)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(NO)(PPh<sub>3</sub>)<sub>2</sub>] (**3ph**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, 500 MHz): δ 7.96 (m, 12 H, PPh<sub>3</sub>), 7.25– 6.90 (m, 18 H, PPh<sub>3</sub>), 2.94 (d, J<sub>HH</sub> = 10.2 Hz, 2 H, C<sub>2</sub>H<sub>4</sub>), 2.91 (t, J<sub>PH</sub> = 31.8 Hz, 1 H, ReH), 2.12 (d, J<sub>HH</sub> = 10.2 Hz, 2 H, C<sub>2</sub>H<sub>4</sub>), 0.68 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 3 H, ReEt), -1.17 (t br, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2 H, ReEt) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K, 125 MHz): δ 136.9 (t, J<sub>PC</sub> = 25.0 Hz, PPh<sub>3</sub>), 134.8 (t, J<sub>PC</sub> = 5.0 Hz, PPh<sub>3</sub>), 131.2 (s, PPh<sub>3</sub>), 128.2–127.5 (m, PPh<sub>3</sub> and C<sub>6</sub>D<sub>6</sub>), 42.9 (s, C<sub>2</sub>H<sub>4</sub>), 20.0 (s, ReEt), 19.0 (s, ReEt) ppm. <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, 200 MHz): δ = 20.4 (d, J<sub>HP</sub> = 31.8 Hz, PPh<sub>3</sub>) ppm.

IR Spectroscopic Data of  $[ReH_2(\eta^2-C_2H_4)(NO)(PPh_3)_2]$  (**2ph**) and  $[ReH(Et)(\eta^2-C_2H_4)(NO)(PPh_3)_2]$  (**3ph**). IR (cm<sup>-1</sup>, KBr pellet): 1959 (m,  $\nu$ (ReH)), 1897 (m,  $\nu$ (ReH)), 1815 (m,  $\nu$ (ReH)), 1630 (s,  $\nu$ (NO)).

[Re( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>( $\eta^4$ -butadiene)(NO)(PPh<sub>3</sub>)] (4ph). A suspension of [ReH( $\eta^2$ -BH<sub>4</sub>)(NO)(PPh<sub>3</sub>)<sub>2</sub>] (1; 0.100 g, 0.13 mmol) in THF (5 mL) was placed in a Young Schlenk tube with a magnetic stirring bar. The Schlenk tube was degassed with three freeze—thaw—pump cycles and charged with 2 bar of C<sub>2</sub>H<sub>4</sub>. The suspension was stirred for 16 h, giving a pale yellow solution. After filtration through a short plug of Celite the volatiles were removed and the crude was triturated with

hexane (3  $\times$  1 mL), yielding analytically pure **4ph** (65 mg, 88%). Crystals suitable for X-ray diffraction were obtained by slowly evaporating a concentrated toluene solution of **4ph**.

IR (cm<sup>-1</sup>, KBr pellet): 1640 (s,  $\nu$ (NO)). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, 500 MHz): δ 7.62 (m, 6 H, PPh<sub>3</sub>), 7.00 (m, 9 H, PPh<sub>3</sub>), 5.75 (q, *J*<sub>HH</sub> = 6 Hz, 1 H, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 5.42 (q, *J*<sub>HH</sub> = 6.5 Hz, 1 H, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 2.50 (t, *J*<sub>HH</sub> = 9.5 Hz, 1 H, C<sub>2</sub>H<sub>4</sub>), 2.23 (m, 2 H, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 2.50 (t, *J*<sub>HH</sub> = 9.5 Hz, 1 H, C<sub>2</sub>H<sub>4</sub>), 2.23 (m, 2 H, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 2.50 (t, *J*<sub>HH</sub> = 9.5 Hz, 1 H, C<sub>2</sub>H<sub>4</sub>), 2.23 (m, 2 H, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), -0.53 (dd, *J*<sub>HH</sub> = 6.5, *J*<sub>IH</sub> = 3.5 Hz, 1 H, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), -1.55 (dd, *J*<sub>HH</sub> = 7.1, *J*<sub>IH</sub> = 3.9 Hz, 1 H, CH<sub>2</sub>=CHCH=CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, 125 MHz): δ 134.2 (d, *J*<sub>PC</sub> = 20 Hz, PPh<sub>3</sub>), 133.6 (d, *J*<sub>PC</sub> = 10 Hz, PPh<sub>3</sub>), 129.9 (d, *J*<sub>PC</sub> = 3 Hz, PPh<sub>3</sub>), 128.9–128 (overlapping m, PPh<sub>3</sub>, C<sub>6</sub>D<sub>6</sub>), 100.8 (s, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 83.0 (s, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 43.5 (d, *J*<sub>PC</sub> = 6.3 Hz, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 31.3 (d, *J*<sub>PC</sub> = 7.5 Hz, C<sub>2</sub>H<sub>2</sub>), 25.3 (d, *J*<sub>PC</sub> = 3.8 Hz, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 25.3 (d, *J*<sub>PC</sub> = 3.8 Hz, CH<sub>2</sub>=CHCH=CH<sub>2</sub>), 300 K, 200 MHz): δ = 22.4 (s, PPh<sub>3</sub>) ppm. Anal. Calcd for C<sub>24</sub>H<sub>25</sub>NOPRe (560.64): C, 51.42; H, 4.49; N, 2.50. Found: C, 51.47; H, 4.49; N, 2.28.

X-ray Diffraction Analysis. Intensity data were collected at 183(2) K on a Xcalibur diffractometer (Agilent Technologies, fourcircle kappa platform, Ruby CCD detector, and a single wavelength Enhance X-ray source with Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å).<sup>26</sup> The selected suitable single crystal was mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction, and analytical absorption correction<sup>27</sup> were performed with the program suite CrysAlis<sup>Pro. 28</sup> The crystal structure was solved with SHELXS-97<sup>29</sup> using direct methods. The structure refinement was performed by full-matrix least squares on  $F^2$  with SHELXL-97.<sup>29</sup> All programs used during the crystal structure determination process are included in the WINGX software.<sup>30</sup> The program PLATON<sup>31</sup> was used to check the result of the X-ray analysis. In the crystal structure of 4ph, all hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and  $U_{iso}(H)$  = 1.2[ $U_{eq}(C)$ ] for aromatic H atoms, with C–H = 0.97 Å and  $U_{iso}(H)$  =  $1.2[U_{eq}(C)]$  for olefinic H atoms. CCDC-854185 contains the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/ data request/cif.

#### ASSOCIATED CONTENT

#### Supporting Information

A CIF file of **4ph** giving further crystallographic data. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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